On the Viscosities of the Hydrogen Halides.

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The measure of agreement between the values of the atomic diameter obtained from W. L. Bragg's crystal measurements, and those deduced from viscosity data and the Kinetic Theory, has recently been demonstrated by A. O. Rankine* for the halogen gas molecules, in which the two atoms are of equal size. The mathematical treatment by which the mean collision area is obtained, can be extended to molecules compounded of two unequal atoms such as those of the hydrogen halides, and the present viscosity experiments were undertaken with a view to affording a test of the further theoretical investigation of Prof. Rankine.†

General Method of Procedure.

The chemical activity of these gases limits the possible modes of measuring the viscosity, and is the cause of the chief difficulties of the experiments. The method chosen was that of the transpiration of the gases through a capillary tube, the dimensions of which were obtained by transpiring air. The viscosity of air is now sufficiently well known to justify its use for this purpose, and the uncertain measurements of the length and diameter of the tube are thus avoided.

The purified gases were first liquefied, and then enclosed and allowed to evaporate. The process of evaporation could be controlled so as to establish a suitable driving pressure, the pressure difference between the ends of the capillary being observed on a liquid U-tube gauge. The masses of gas passing were measured by absorbing in water and titrating with standard alkali. The corresponding volumes were obtained from density data.

Experiments were performed at two temperatures, the interval being about 85° C. This enables Sutherland's constant to be calculated for these gases.

Determination of the Constant of the Tube.

The capillary tube was selected from many that were calibrated. That ultimately chosen was 80 cm. in length, the maximum variation being less than $\frac{1}{2}$ per cent. of the mean diameter, which was 0·0342 cm. (found by weighing a thread of mercury filling this length). The order of diameter suitable for the proposed method of establishing the pressure difference was previously ascertained by trial with various tubes.

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* 'Roy. Soc. Proc.,' A, vol. 98, p. 360.

† 'Phys. Soc. Proc.,' June, 1921.

The form of the apparatus is shown diagrammatically in fig. 1. Air is drawn through the capillary tube by means of an aspirator, the volume of water run off giving, after several corrections, the volume of air passing. The end B is open to the atmosphere through drying tubes containing (1) calcium chloride and soda-lime; (2) phosphorus pentoxide; and (3) glass-wool. The spiral F, made of about a metre of 5-mm. tubing, sealed on to the experimental tube and enclosed in the same jacket, ensures that the air enters the capillary at the temperature of the jacket, at least for the rates of flow used, which amounted to only a few cubic centimetres per minute. The pressure difference is read on a sulphuric acid gauge, one limb of which was connected at C, while the other is open to the atmosphere. The density of the acid was found, and conveniently checked from time to time by comparison with a distilled water gauge, placed temporarily in parallel at the four-way piece, C. As a mean of seven readings at various pressure differences, the value found was 1·840 ± 0·0004 times the density of water in the neighbourhood of 20° C.

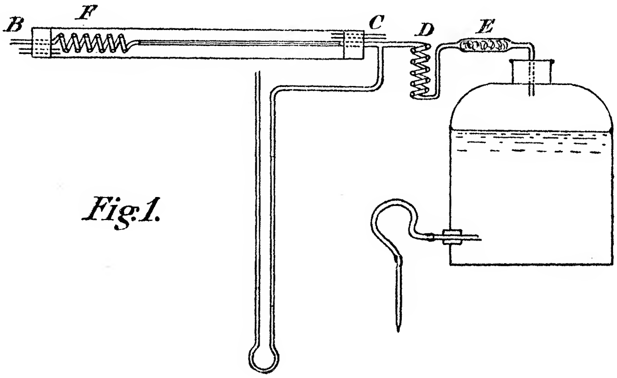

Fig. 1.

As the aspirator was at room temperature (usually above the temperature of the jacket), the spiral D was inserted and kept immersed in a beaker of water at room temperature. The tube E contains calcium chloride, to protect the capillary tube from water vapour drawing back. The aspirator had an area of cross-section of about 700 square cm., so that the pressure head varied but slightly during a collection lasting, say, 15 minutes. Variations in the pressure head were conveniently made between wide limits, without necessitating a very large aspirator, by varying the height of a nozzle attached by pressure tubing to the exit tube.

Meyer's transpiration formula,

$$P_1V_1 = P_2V_2 = \frac{(P_1^2-P_2^2)\pi a^4}{16l\eta},$$

can be written

$$\eta = \frac{(P_1-P_2)(P_1+P_2)}{16l\,P_2V_2} = \frac{\delta(2P_1-\delta)}{(P_1-\delta)V_2}\,\frac{60g\,\rho_0\pi a_4}{16l},$$

where δ = pressure difference (obtained from gauge readings).

P_1 = atmospheric pressure $= P_2+\delta$, all measured in centimetres of mercury at 0° C., and ρ_0 = density of mercury at 0° C.

V_2 = volume of dry air passing per minute at pressure, P_2, and temperature of the jacket, t_c.

In the experiments, the volume of water collected gives the increase in the volume of saturated air in the aspirator, at pressure P_2, and temperature, t_a. Two corrections have therefore to be applied. Volume V_2, on entering the aspirator, is raised from t_c to t_a. Further, it has become saturated (this assumption is probably correct for the small rates of flow used). Since the total pressure, P_2, remains constant, the partial pressure of the air in the aspirator is less than P_2 by the saturation vapour pressure of water at t_a, and the air accordingly expands, so that if V = observed volume of water displaced per minute, after correction for the temperature,

$$V_2 = \frac{P_2-\sigma}{P_2}V = \frac{P_1-\delta-\sigma}{P_1-\delta}V.$$

Substituting in the equation for η,

$$\eta = \frac{60g\rho_0\,.\,\pi a^4}{16l}\cdot\frac{\delta(2P_1-\delta)}{(P_1-\delta-\sigma)V} = K\frac{\delta(2P_1-\delta)}{(P_1-\delta-\sigma)V}$$

where K contains all constant quantities, so that if δ, P_1 and σ are in centimetres of mercury at 0° C., V in cubic centimetres per minute at P_2 and t_c, the equation gives the viscosity. The values of η_{air}, used in calculating K, are the most recent of Prof. Rankine, viz.,

$$\eta_0 = 1{\cdot}724\times10^{-4} \text{ C.G.S. units,}$$

$$\eta_{15} = 1{\cdot}799\times10^{-4} \quad \text{,,}$$

In setting up the apparatus for the determination of K, glass joints were made throughout (except the connection to the aspirator, which, however, was well waxed) to prevent leak. A preliminary experiment was made to ascertain the limit of steady flow before turbulence sets in for the tube in use. We have

$$V_2 \propto \delta\frac{(2P_1-\delta)}{P_1-\delta},$$

i.e.,

$$V_2 \propto 2\delta\left(1+\frac{\delta}{2P_1}\right) \text{ approximately.}$$

It was found that, up to about 60 cm. sulphuric acid, the values of V_2, plotted against $\delta(1+\delta/2P_1)$, gave a straight line, showing that the condition of steady flow obtained.

Several sets of determinations of K were made during the course of the experiments upon the gases, varying the pressure difference over the range from 10 to 40 cm. sulphuric acid. The constancy of K throughout showed that it was independent of the set-up of the apparatus, and therefore that there was no leak, and at the same time confirms that the region of velocities used was that of steady flow.

The temperature of the jacket was maintained constant by passing a rapid stream of water through it, and was recorded as the mean of the inlet and outlet temperatures, measured with mercurial thermometers graduated in 1/10° C. A third thermometer, suspended within the aspirator, gave t_a. All three were compared with a standard thermometer which had been recently calibrated, and their lower fixed points were checked.

The volume of water collected in a known time was found by weighing, correcting for buoyancy and the density of water. The times were measured with a stop-watch, which was used throughout the experiments.

The disadvantage of this method of determining K is that variation in temperature of the aspirator during an experiment will affect the volume of water collected. The error was minimised by wrapping the aspirator in cotton-wool and leaving it for some hours after setting up, in order that a steady temperature might be reached before beginning the measurements. The temperature was then taken at intervals and the pressure difference also observed, the means being used in the calculations.

Table I.

t ° C.	K × 10^4.	t ° C.	K × 10^4.	t ° C.	K × 10^4.
10·0	1·7076 1·7044 1·7077 1·7078 1·7026	9·5	1·7073 1·7093 1·7085	19·0	1·7057 1·7045 1·7116 1·7117 1·7064
Means	1·7060		1·7084		1·7080

Table I records the values of K obtained in three sets of experiments, taken before and after the HCl experiments, and with bromo-naphthalene in the gauge preparatory to the HBr experiments.

At steam temperature K will have a slightly increased value, on account of the expansion of the capillary. This has been deduced by assuming the coefficient of linear expansion of glass to be 0·000009.

The mean value of K_{19} is $1{\cdot}7076 \pm 0{\cdot}00005 \times 10^{-4}$. As a check upon this figure, the value of K was also calculated from the dimensions of the tube.

Approximate length of capillary = 78·4 cm.
„ diameter „ = 0·0342 cm.

The value thus obtained was $K = 1{\cdot}705 \times 10^{-4}$, and the agreement to 0·15 per cent. is satisfactory.

Hydrogen Chloride.—Description of Apparatus.

The apparatus used for the viscosity of hydrogen chloride is shown in fig. 2. The gas was prepared by dropping concentrated sulphuric acid on pure sodium chloride, and was dried by passing over P_2O_5 in a metre length of ½-inch tubing, entering the apparatus at tap T_2. After having displaced air from the apparatus, the bulb A was surrounded by liquid air, the flask being lowered occasionally to allow the solid HCl to liquefy and collect in the bulb.

The form of the pressure gauge designed for these experiments is clear from fig. 2. The U is connected below to a bulb, and then by flexible tubing to a mercury reservoir. The gauge liquid (sulphuric acid for HCl) rests on mercury, and by raising or lowering the reservoir can be made to stand at any point in the gauge tubes; or it can be lowered beyond the U, so that air can be swept from the connecting tubes.

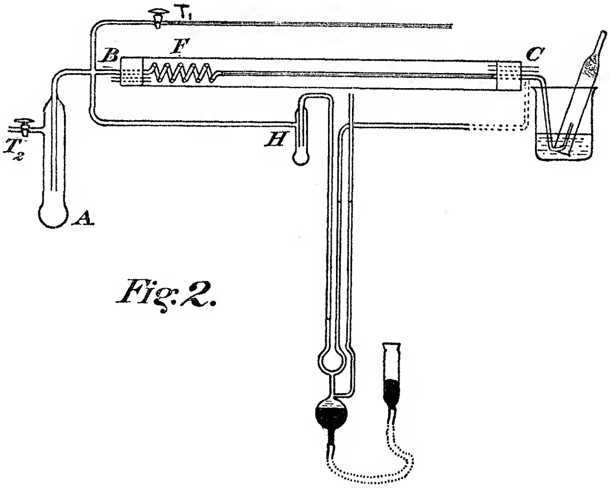

Fig. 2.

The gauge was originally connected at B and C, while the third limb shown was open to the atmosphere; but with the method of collection described below, this third limb indicated that connection to C was unnecessary, as the pressure there remained atmospheric. The trap H was added to prevent the gauge liquid from being drawn back into the apparatus with the sudden variations of pressure when liquefying the gas. It was found convenient to have the capillary and tap T_1 closed, with a few centimetres of liquid in the U of the gauge; this indicated the variations of pressure and made it possible to generate the gas at such a rate that practically all was liquefied.

An auxiliary capillary tube was connected at B in parallel with the experimental one through tap T_1. Its inclusion gives a ready means of varying the pressure difference across BC by altering the length in circuit. This arrangement works more satisfactorily than a tap.

When the steady pressure difference is established (see later), a means is required of absorbing the gas in water for a definite time and which will not disturb the pressure at C. The following simple arrangement was proved to satisfy both conditions. The exit tube is drawn out and bent as shown; at the required moment a test-tube, drawn out and open to the atmosphere at its upper end through a plug of moistened glass wool, was clapped over the nozzle and at the same moment a beaker of water was brought up into position from below. Moistened blue litmus-paper placed upon the open end of the test-tube showed that no gas escaped beyond the glass wool. At the end of the required time the test-tube was raised and the beaker lowered simultaneously, and with the exit nozzle shaped as shown, very little water adhered to it. The acid from the test-tube was washed into the beaker and the whole acid titrated with N/10 KOH, using phenol phthalein as indicator, or N/10 Na_2CO_3, using methyl orange.

The Viscosity Experiment.

When about 10–15 c.c. of liquid HCl had condensed in the bulb A, the tap T_2 was closed and the generating apparatus removed. The liquid air flask was lowered until sufficient gas had passed over to sweep all air from the apparatus, the gauge liquid being lowered to clear its tubes and then raised to send a rapid current of gas through the capillaries. The bulb A was then surrounded by an empty Dewar flask and the whole heavily wrapped in cotton wool. It was found that the rate at which the gas evaporated from the liquid HCl soon settled down to a constant and measurable value, depending on the small amount of heat reaching the bulb. By varying the length of the auxiliary capillary tube in parallel with the experimental one, the pressure differences between B and C could be reduced to any desired value suitable for a viscosity measurement. This pressure difference remained remarkably steady and only varied gradually, usually by less than 1 per cent., during the 10–20 minutes taken for an experiment. During the initial stages, however, sudden fluctuations of several per cent. occasionally occurred, perhaps as bubbles of gas rose to the surface in bulb A. This was noticed more particularly at the lower temperature experiments. By observing the pressure difference every 2 minutes, the mean value is obtained in which these variations are unimportant.

Several series of experiments were made at the temperature of the water supply and at steam temperature, varying the pressure difference, but keeping well within the limits of steady flow for air. When the time of collection of the gas was varied, no systematic error due to end-effects could be detected. The initial and final portions of gas coming over from A were neglected as possibly containing impurity. A test of the purity of the gas was made by collecting a sample over dry mercury; when a little water was inserted, the whole of the gas dissolved.

The transpiration formula in this case gives

$$\eta_t = \mathrm{K}_t \frac{(\mathrm{P}_1-\mathrm{P}_2)(\mathrm{P}_1+\mathrm{P}_2)}{\mathrm{P}_2\mathrm{V}_2} = \mathrm{K}_t \frac{\delta(2\mathrm{P}_2+\delta)}{\mathrm{P}_2\mathrm{V}_2}$$

where P_2 = atmospheric pressure $= \mathrm{P}_1-\delta$.

As before, P_2 and δ are converted to centimetres of mercury at 0° C. The appropriate value of the constant is obtained from the experimental value, using the formula

$$\mathrm{K}_t = \mathrm{K}_0(1+3\gamma t) \quad \text{where} \quad \gamma = 0{\cdot}000009.$$

The volume of gas (V_2) at pressure P_2 and the temperature of the jacket is calculated from the weight of gas deduced from the titration results; and here enters probably the greatest error of the method. For the molecular weight density is certainly too low, owing to slight departures from perfect gas laws even at ordinary temperatures. The experimental density at 0° C. as given by Guye and Gazarian (Kaye and Laby's Tables) is therefore assumed, and the constants of Van der Waal's equation (Dewar, 1884) used to obtain the density at the required temperatures, this being considered the best approximation available. The data used are:—

Experimental density at 0° C. and 760 mm. = 1·6399 grm. per litre.
Van der Waal's constant, a = 0·00697,
" " b = 0·00173.

The volume of gas (v) under pressure P_2 and at the jacket temperature t_c equivalent to 1000 c.c. N/10 solution is the quantity entering directly in the calculation of η and the values used for the two sets of experiments recorded in Table II are given below:—

At 12·5° C. and 759·6 mm., $v = 2326$ c.c. per litre.

At 100·3° C. and 768·8 mm., $v = 3014$ „

(The molecular weight values are 2343 c.c. and 3026 c.c. respectively.)

The means of the sets of viscosity results at 12·5° C. and 100·3° C. recorded in Table II are used to calculate Sutherland's constant C, from the expression,

$$\frac{\eta_2}{\eta_1} = \left(\frac{T_2}{T_1}\right)^{3/2} \left(\frac{C+T_1}{C+T_2}\right).$$

Table II.

t ° C.	$\eta_t \times 10^4$.	t ° C.	$\eta_t \times 10^4$.	Sutherland's constant C.
12·5	1·398 1·385 1·399 1·373 1·389 1·414	100·3	1·838 1·836 1·838 1·840 1·837	
Means	1·397 ±0·003		1·838 ±0·0004	357

The method has the advantage that a steady continuous flow is attained which allows the quantities involved to be measured with considerable accuracy. The least accurate is the titration; it was convenient, however, to run the experiment for a sufficient time to collect an amount of gas equivalent to 50–60 c.c. N/10 solution, and this can be titrated to an accuracy of 0·1 c.c. or 1 part in 500; and this also seems to be the order of accuracy indicated in the final mean values of the viscosity, by application of the recognised rules for estimating probable errors.

Hydrogen Bromide.

The gas was prepared by dropping bromine on a mixture of red phosphorus, sand and water, and was freed from bromine vapour by passing through a U-tube containing moist glass wool mixed with red phosphorus, drying over P_2O_5 as before.

The experiment was carried out exactly as for hydrogen chloride, except that another gauge liquid was required, since sulphuric acid is attacked by HBr. Bromonaphthalene was selected as a suitable liquid for a gauge, the density being found by comparison with a water gauge in parallel. As a mean of seven readings at different pressures, the density was 1·5175 ± 0003 times the density of water in the neighbourhood of 20° C. In this case, as indeed in the previous experiment, the gas dissolves to some extent in the gauge liquid, but as the area of contact is small, the alteration in density is negligible, especially for the liquid in the further column which measures δ.

Accurate experimental data for the density of hydrogen bromide for the calculation of V_2 are not available, the only estimates being those of Biltz (1892) and Strecker (1882). The experimental measurement was, therefore, undertaken.

Density of HBr.

A metre length of $\frac{3}{4}$-inch tubing was drawn out at the ends and taps sealed on, the tube being enclosed in a jacket for water or steam. It was evacuated, connected to T_1 (fig. 2), and filled with the gas prepared and liquefied as above. Both taps were then opened, and a vigorous current of gas passed over from A to sweep out last traces of air. The purity of the issuing gas was tested by collecting a sample in a large test-tube over mercury ; when a little water was inserted the whole of the gas dissolved except for a minute bubble which might possibly have been hydrogen as the mercury surface was badly fouled.

When satisfied that all air had been driven out, the taps were closed leaving the pressure inside greater than atmosphere, and a stream of water was passed through the jacket until a steady temperature had been reached, when one tap was opened for a moment, gradually to avoid oscillations, thus establishing atmospheric pressure inside. One end of the tube was then opened under water, which rose owing to absorption, and the whole of the gas was carefully absorbed and washed into a beaker, titrating with N/10 KOH as in measuring the volumes in the viscosity experiments. The volume of the tube between the taps was measured by weighing the distilled water filling it and was 229·6 c.c. at 20·4° C.

In this way the density of HBr was measured at both water and steam temperatures. Though the method makes no claim as an accurate absolute determination, it at least affords a means of passing back from volumes of N/10 solution to volumes of gas, especially as the gas was prepared in the same way in both viscosity and density experiments.

The density proved to be greater than the molecular weight value, as indeed would be expected. According to Hautefeuille* dissociation does not begin until above 700° C. The values of v deduced from the density experiments are as follows:—

At 18·7° C. and 762·2 mm., $v = 2370$ c.c. per litre N/10.
At 100·0° C. and 760·1 mm., $v = 3046$ c.c. „ „

(The molecular weight values are 2379 c.c. and 3059 c.c. respectively.)

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* 'Compt. Rend.,' 1867.

In Table III the results of several sets of viscosity experiments are recorded, those at the lower temperature all being reduced to 18·7° C. to give the mean used in calculating Sutherland's constant C.

Table III.

t ° C.	$\eta_t \times 10^4$.	$\eta_{18\cdot7} \times 10^4$.	t ° C.	$\eta_t \times 10^4$.	Sutherland's constant C.
18·3	1·831	1·834	100·2	2·364	
17·9	1·810	1·815		2·358	
	1·838	1·843		2·365	
	1·824	1·829		2·372	
	1·829	1·834			
18·7		1·840			
		1·857			
		1·835			
		1·845			
		1·817			
18·7	Means	1·835 ±0·0027	100·2	2·365 ±0·0019	375

Hydrogen Iodide.

The gas was prepared by dropping water on a mixture of pure re-sublimed iodine and red phosphorus, and was liquefied in bulb A after passing over red phosphorus and P_2O_5 as for HBr. Some difficulty was experienced in finding a suitable gauge liquid; bromonaphthalene dissolved the hydrogen iodide freely and very soon it decomposed, giving a dense coloration of iodine, which proceeded to attack the mercury. Oils containing unsaturated hydrocarbons are useless as they are all attacked by HI.

The difficulty was finally surmounted in the following way. A length of about 70 cm. of 1-mm. capillary tubing was inserted between B and H (fig. 2), with a vertical spiral of 5-mm. tubing on the side nearest B. Air was allowed to remain on the side of the capillary nearest the gauge, and bromonaphthalene was again used as the liquid. Then, during the course of an experiment, only the HI that diffused along the capillary could reach the gauge and most of this dissolved in some of the bromonaphthalene placed in the bulb H. It was found that the liquid in the gauge tubes remained free from contamination for hours, though the liquid in H became deeply coloured with iodine. The spiral was inserted so that any small quantity of air diffusing backwards through the capillary would have a greater distance to travel before reaching B.

With this modification of the apparatus, the viscosity experiments were carried out exactly as for the other gases, titrating with the same standard solutions. On account of the slow decomposition of HI in sunlight, the whole experiment was performed in the dark,* using electric light only when required to take readings. Decomposition with heat proceeds but slowly below 180° C. (Hautefeuille). In view of the above circumstances, it is probable that the results for HI are not quite so reliable as those for HCl and HBr.

The set of values of η, at the lower temperature recorded in Table IV, obtained with varying pressure differences, as always, is evidence that the difficulties had been practically overcome. But at the steam temperature a new difficulty presented itself. The calculated value of η decreased in a regular manner during the two hours over which the experiments extended, and it was noticed that at one point of the experimental capillary there was a fine yellow deposit, probably of a volatile phosphorus compound. Some iodine was also at first deposited where the tube left the steam-jacket, but after some time this disappeared. It was considered that the most satisfactory way of ascertaining the new constant of the tube was to redetermine η at the lower temperature without interrupting the flow of gas. This was accordingly carried out immediately after the last determination at steam temperature, and the value of η found was $1{\cdot}842 \times 10^{-4}$, as compared with $1{\cdot}873 \times 10^{-4}$ previously. The difference is of the same order as the decrease in η_{100} during the set of readings, and indicates a gradual increase in the apparatus constant. The observed mean of η_{100} was therefore corrected by inserting the probable mean value of the constant at the time of the observations. Whatever the cause of the regular increase in the apparatus constant, this method of correction certainly eliminates the error more nearly than by redetermining it with air.

The density of hydrogen iodide was found experimentally by the method previously described, and, owing to the greater uncertainty in the molecular composition of this gas, especially at 100° C., the necessity for doing so is still greater. The values obtained and used in the calculation of η are as follows:—

At 20·6° C. and 765·1 mm., $v = 2353$ c.c. per litre N/10.
At 100·2° C. and 766·1 mm., $v = 2292$ c.c. " "

(The molecular weight values under these conditions are 2392 and 3037 c.c. respectively.)

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* Lemoine, 'Compt. Rend.,' vol. 85, p. 144 (1877).

Table IV.

t °C.	$\eta_t \times 10^4$.	t °C.	$\eta_t \times 10^4$.	$\eta_{100\cdot2} \times 10^4$, corrected.	Sutherland's constant C.
20·6	1·879 1·871 1·865 1·873 1·877	100·2	2·396 2·391 2·388 2·387 2·387 2·373 2·372		
Means ...	1·873 ±0·0016		2·385 ±0·0023	2·404 ±0·0023	390

Summary of Results.

The results for the three gases are summarised in Table V, the values of C being used to extrapolate over the small ranges to η_0 and η_{100} from the experimental data.

Table V.

	$\eta_0 \times 10^4$.	$\eta_{100} \times 10^4$.	C.
HCl	1·332	1·837	357
HBr	1·710	2·365	375
HI	1·731	2·403	390

In conclusion, I wish to express my gratitude to Prof. Rankine for helpful suggestions and for the kind interest he has taken in this work.